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Structure and reconfiguration of epitaxial GeTe/Sb₂Te₃ superlattices

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Summary

Phase-change materials based on GeSbTe show unique switchable optoelectronic properties and are an important contender for next-generation non-volatile memories. They are particularly attractive as a universal storage-class memory, which is an intermediate solution having properties between the speed of DRAM and non-volatility of Flash. Their change in dielectric properties is currently also being exploited for novel optical applications such as displays and photonic memories, having possibilities such as smart glasses and displays and non-von-Neumann computing. In 2011 a breakthrough was established in the field of phase-change memories when it was shown that growing GeTe and Sb₂Te₃ superlattices showed significantly improved performance compared with conventional mixed GeSbTe alloys, having lower programming currents, higher switching speed and better durability. Although the details were unclear then, this improvement was ascribed to a switching mechanism that happened within the solid state of the material. To grow and understand such superlattices has been an important motivation for the EU PASTRY project and this thesis, where the research was conducted with 6 independent partners. Our contribution as a partner and thus this thesis focuses particularly on the structural characterization of GeTe-Sb₂Te₃ superlattices using transmission electron microscopy. Different growth techniques have been applied, including the high-quality research oriented molecular beam epitaxy and industrially applicable sputtering physical vapor deposition.

Chapter 1 starts out with introducing the thesis' research in the context of phase-change materials and phase-change memory applications, although the material class is certainly relevant for other fields such as thermoelectrics and topological insulators. It describes how, historically, Te based alloys were discovered to show electrical resistance switching phenomena after which the most common phase-change alloy GeSbTe is discussed. The chapter continues to discuss the crystallographic structures and bonding anisotropy of GeSbTe, particularly on the GeTe-Sb₂Te₃ tie-line, which turned out to be necessary prerequisites for

understanding the growth of epitaxial phase-change materials. The chapter finishes with an outline of this thesis and a short introduction of the following chapters.

Chapter 2 continues with the experimental methods which are relevant for this thesis and is split up into two parts. The first part treats some of the general aspects of high-energy electron characterization and continues with transmission electron microscopy techniques which are relevant for the work in this thesis. High resolution transmission electron microscopy and scanning transmission electron microscopy are then discussed in detail. The second part then continues with specimen preparation for the transmission electron microscope, which is at least equally important to obtain useful results and meaningful analyses. In the end the specific specimen preparation recipes are outlined, which could be used as a reference for future work.

In Chapter 3 the first successful analyses of epitaxial GeTe-Sb₂Te₃ superlattices are shown, as performed in this project, establishing the essential research techniques paramount for this thesis. The growth and characterization of the samples is done by molecular beam epitaxy and cross section transmission electron microscopy, respectively. Although the GeTe or Sb₂Te₃ sublayer thicknesses applied are relatively thick, between 3 nm and 12 nm, the techniques mark an important step for the continued development of ~1 nm thinner layers, necessary for superlattice phase-change memories. Two types of Si(111) surfaces were used, the bare (7×7) reconstructed surface and complete Sb-terminated surface. It is shown that highly-textured multi-layers can be grown and that compositional analysis based on energy dispersive X-ray spectroscopy allows accurate quantification of the average GeTe and Sb₂Te₃ sublayer thicknesses.

The results in Chapter 4 mark a successful breakthrough in the field of superlattice phase-change memories, as they show that both high-quality growth and characterization can be performed. Also, they shed new light on the interface formation between GeTe and Sb₂Te₃, contradicting some of the previously proposed models in the literature. Epitaxial GeTe-Sb₂Te₃ superlattices were grown on passivated Si(111) at temperature ranging from 210°C to 230°C using molecular beam epitaxy and sputtering physical vapor deposition, and they have been characterized particularly with cross-sectional transmission electron microscopy.

Contrary to the previously proposed models, it is found that the state of the films actually crystallizes as van der Waals bonded layers (i.e. a van der Waals heterostructure) of Sb_2Te_3 and trigonal GeSbTe . Moreover, it is shown by annealing the films at 400°C , which reconfigures the superlattice into bulk trigonal GeSbTe , that this van der Waals layer is thermodynamically favored. These results are explained in terms of the bonding anisotropy of GeTe and Sb_2Te_3 and the strong tendency of these materials to intermix. The findings thus debate the previously proposed switching mechanisms of superlattice phase-change materials and give new insights in their possible memory application.

Chapter 5 then extensively and quantitatively characterized the van der Waals layer distribution in $\text{GeTe-Sb}_2\text{Te}_3$ superlattices, both their formation after MBE growth at 230°C and after annealing at 250°C , 300°C and 400°C . The thermal reconfiguration is also particularly important in the context of the vacancy ordering process in GeSbTe , which is responsible for both an electronic metal-insulator transition and a structural cubic-to-trigonal transition. $\text{GeTe-Sb}_2\text{Te}_3$ based superlattices, as shown in the previous chapter, provide an interesting platform for the study of GeSbTe alloys. It is shown that the van der Waals gaps in these superlattices, which result from vacancy ordering, are mobile and reconfigure through the film using bi-layer defects and Ge diffusion upon annealing. Moreover, it is shown that for an average composition that is close to GeSb_2Te_4 a large portion of 9-layered van der Waals systems is formed, suggesting that still a substantial amount of random vacancies must be present within the trigonal GeSbTe layers. Overall these results illuminate the structural organization of van der Waals gaps commonly encountered in GeSbTe alloys, which are intimately related to their electronic properties and the metal-insulator transition.

In Chapter 6 the epitaxy of exemplary chalcogenides Sb_2Te_3 and GeTe on different surfaces of $\text{Si}(111)$ with atomically sharp interfaces is presented and compared using plan-view transmission electron microscopy and electron diffraction. It is shown that depending on the monolayer surface termination the resulting films present drastic differences in terms of film morphology and crystallinity. In particular, a profound difference is found between the films grown on H-passivated and Sb-passivated surfaces. In both cases, the out-of-plane texture

is strongly c-axis oriented, but the case of Si(111)-H shows the frequent occurrence of random in-plane twist for both films, while for Si(111)-Sb this is strongly suppressed. The role of the substrate-film interface for the epitaxy is discussed and the consequences for the properties of the films are highlighted. In general, the insights of these results shed light on chalcogenide thin film growth for topological insulator, ferroelectric, thermoelectric and phase-change materials research.

Hence, the work in this thesis has demonstrated several important aspects of the growth of nanostructured GeTe-Sb₂Te₃ phase-change materials. One of the findings is that these superlattices, when grown in the epitaxial regime, actually form superlattices of Sb₂Te₃ and trigonal GeSbTe van der Waals layers. The proposed structure proves a good starting point for unraveling the switching mechanism of GeTe-Sb₂Te₃ superlattices. Also, this implication opens another option for the growth of these materials by directly depositing Sb₂Te₃ and trigonal GeSbTe, which is a route pursued by some of our partners. The other important finding of this work is the thermal reconfiguration of the superlattices into the mixed GeSbTe alloy. It shows the thermal balance which has to be maintained during growth, where on the one side high temperature is needed to achieve high-quality textured films, but on the other hand not too high as to avoid complete mixing. Also, in industrial implementation of such materials this thermal reconfiguration poses a difficulty, as many production line techniques do require high temperature in their production steps. And finally, although the switching mechanism of superlattice phase-change memories is not resolved during the time of this project, and new hypotheses have been proposed in the field, HAADF scanning transmission electron microscopy proves essential to unravel the mechanism. In order to unravel the (two) distinct memory structures, very delicate and advanced specimen preparation techniques should be used of actual devices using particularly the focused ion beam, where care should be taken not to heat the specimen too much. This still remains an open question for future research.